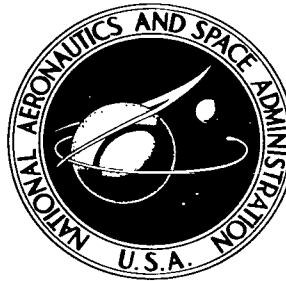


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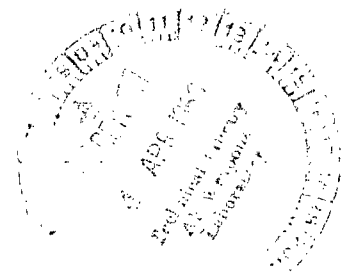


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IONIC CONDUCTIVITY OF SOLID BARIUM FLUORIDE

by William L. Fielder
Lewis Research Center
Cleveland, Ohio



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SUMMARY

The conductivities of barium fluoride single crystals were observed from about 160° to 890° C. Three regions were observed: (1) extrinsic, (2) lower intrinsic, and (3) upper intrinsic.

In the extrinsic region (impurity controlled), the specific conductivity K_s of each crystal may differ. Two crystals gave the following rate equations:

$$K_s = 0.58 \exp \left(-\frac{22\,000}{RT} \right) \quad \text{ohm}^{-1} \text{ cm}^{-1}$$

$$K_s = 1.3 \exp \left(-\frac{23\,000}{RT} \right) \quad \text{ohm}^{-1} \text{ cm}^{-1}$$

where R is the gas constant (calories per degree) and T is the absolute temperature.

All four crystals gave essentially the same conductivity for the intrinsic regions. The two rate equations for the lower and upper intrinsic regions are, respectively,

$$K_s = 3.78 \pm 0.09 \times 10^4 \exp \left(-\frac{32\,700 \pm 500}{RT} \right) \quad \text{ohm}^{-1} \text{ cm}^{-1}$$

$$K_s = 2.05 \pm 0.03 \times 10^5 \exp \left(-\frac{35\,600 \pm 500}{RT} \right) \quad \text{ohm}^{-1} \text{ cm}^{-1}$$

The thermally produced defects, responsible for the conductivity of solid barium fluoride in the intrinsic region, are suggested to be fluorine ion vacancies and fluorine ions in interstitial sites. These defects may be produced by impurities in the extrinsic region.

Finally, activation energy requirements were related to a suggested mechanism. In the intrinsic region, it is suggested that defects of fluorine ion vacancies and interstitials are formed with a formation energy of about 20 kilocalories. In the lower intrinsic region, migration of the fluorine ion vacancies can occur with a migration energy of about 23 kilocalories. In the upper intrinsic region, migration of the fluorine ions in the interstitials may become increasingly more important with a migration energy of about 26 kilocalories.

INTRODUCTION

Solids are often considered to be either metallic, semiconductors, or insulators. This suggests that a current is carried through a solid only by means of electrons. This simple classification, however, is inadequate. Ionic solids may also conduct partially or completely by an ionic mechanism.

Ionic conductivity in solids was observed as early as 1888 by Curie (ref. 1), and the migration of ions through certain solids according to Faraday's law was clearly shown by transference number investigations; for example, solid sodium chloride conducts ionically at 425° C by migration of the sodium ions (ref. 2).

Most of the investigations, concerned with the conductivity of ionic solids, have dealt primarily with certain oxides and with the halides of group I (alkali metals, ref. 3) and of group IB (copper and silver, ref. 4). Similar to groups I and IB, group II (magnesium, calcium, strontium, and barium) halides also should function as ionic conductors; however, the conductivity for this group has been observed in calcium fluoride only (ref. 5). It was also concluded that transition metal oxides are more likely to conduct by means of electrons even though the oxide may be ionic in character. The ionic contribution in these oxides may become more significant under certain conditions: (1) if the lattice structure is altered by impurities (e. g., calcium oxide into zirconium oxide), and (2) if the number of defects leading to ionic conductivity is increased (e. g., by doping).

The purpose of this investigation was threefold. First, an attempt was made to improve the overall accuracy of the conductivity measurements. Most of the previous determinations have been relatively inaccurate. Some of the following may have contributed to these inaccuracies: (1) use of crystals of insufficient purity, (2) use of polycrystalline samples which led to undesired surface effects, (3) use of direct current which led to polarization effects, (4) use of improper contacts in alternating current which also led to polarization effects, (5) inadequate temperature control, and (6) use of bridges of only moderate accuracy.

Second, the conductivities of four barium fluoride single crystals were to be determined over a wide temperature range of 160° to 890° C. Although considerable information is available concerning the simpler structured alkali metal and silver halides, less is known for other halides. Group II halides are of particular interest since they are divalent and more complex in structure. Furthermore, the conductivity of the Group II fluorides should be predominately anionic (ref. 2). Thus, the interpretation of the fluoride conductivities may be simplified somewhat since only one ion is migrating. Additional considerations led to the investigation of barium fluoride. It is conceivable that barium fluoride may serve as a fluorine ion conductor (solid electrolyte) in power generation systems.

Third, the energy requirements (A-factor and activation energies) for the conductivity of barium fluoride were to be calculated and related to some possible mechanisms suggested for the condition.

EXPERIMENTAL

Barium Fluoride Crystals

Single crystals of pure barium fluoride were investigated. A random analysis of the single crystals is shown in table I. Surface irregularities were removed by grinding the crystals and then polishing them with anhydrous ethyl alcohol. The resulting crystals were colorless and transparent and contained no internal flaws that were visible to the eye. All subsequent crystal manipulations were performed under anhydrous conditions to minimize absorption of water on the crystal surfaces. The faces used for the resistance measurements were 111 planes such as indicated by X-ray analyses.

For accurate resistance measurements, the crystal dimensions must be measured accurately. The general equation is

$$R_S = \frac{R_T A}{L}$$

where

R_S specific resistance, ohm-cm

R_T total resistance, ohm

A area, cm^2

L length, cm

Although the crystal cubes (about 1.3 by 1.3 by 1.3 cm) could be measured to an accuracy of about 0.05 percent at room temperature, determining the area and the length with equal accuracy at the temperature that the resistance measurement was made is more difficult. A correction was made for all temperatures by assuming a coefficient of thermal expansion of 1.84×10^{-5} per $^{\circ}\text{C}$ per centimeter (ref. 6).

If the crystals are not properly surface coated, an excessive polarization effect may be observed that leads to erroneously high resistance values even for alternating-current measurements. Two coatings were used with reasonable satisfaction. One coating consisted of a layer of platinum on both crystal faces that had been sputtered on in the ab-

sence of air or oxygen. The second coating consisted of several thin coats of a thin emulsion of colloidal graphite and absolute alcohol painted on the two faces. The alcohol is then removed in vacuum at higher temperatures. In general, the platinum-sputtering technique was superior to the latter technique for most of the alternating-current measurements since only small changes in the resistance were observed for the different frequencies (100 cps, 1 kcps, and 10 kcps). Graphite coatings led to a considerable increase in the resistance (polarization) for the lower 100-cps and 1-kcps frequencies at higher temperatures. Fortunately, these polarization effects are negligible for graphite surfaces at 10 kcps since platinum-sputtered surfaces could not be used above about 680° C. In addition, graphite contacts were used for direct-current resistance measurements below 300° C since they were simpler to prepare.

Resistance Measurements

Direct current was used for some of the previous resistance measurements of ionic solids. Some of this work found in the literature may be either unreliable or questionable because of the polarization effects encountered. For example, the direct current resistance of silver bromide between gold electrodes is about 20 times the alternating current resistance after 15 seconds and about 100 times it after about 3 minutes (ref. 7). The more recent investigations have used alternating-current impedance bridges.

This investigation uses both direct and alternating currents. The direct-current system, consisting of an electrometer, was used for resistance values ranging from 10^8 to 10^{11} ohms because the alternating-current method could not operate in this range. The accuracy of the electrometer is about 5 percent of full scale. Although the electrometer can be used up to about 10^{14} ohms (guarded), the barium fluoride crystals were observed only to about 10^{11} ohms since the apparatus contributed a parallel resistance of about 10^{12} ohms to the single crystal.

The bulk of the resistance measurements were made by means of the alternating-current method. The instrument was an impedance comparator, which consists essentially of a single source, a current detector, and two highly precise bridge arms. The signal source can be adjusted to either 100 cps, 1 kcps, or 10 kcps. The other two bridge arms are external. One external arm contains the crystal and the other contains adjustable standard resistors in series with adjustable capacitors. Any unbalance in either the impedance (0.01 percent) or the phase angle (0.0001 radian) of the two external arms is given by the comparator.

Since the two internal bridge arms are more accurate than the external arms, the overall accuracy of the bridge readings may depend largely on the external arms. Two decade resistors were used in series so that values ranging from 10^6 to 0.1 ohm could be

observed. The direct-current resistance for these resistors is stated as accurate to within 0.05 percent, and they are specially designed to minimize frequency error in alternating current use. The other external arm contained the barium fluoride crystal, electrodes, and leads. This arm can be represented as capacitance in parallel with the resistance of the crystal and leads. The crystal (and lead) resistance can be assumed to be equal to the resistance of the decade resistors with reasonable accuracy up to values of about 4×10^5 ohms for 100 cps and 6×10^4 ohms for 10 kcps. For smaller resistance values (less than 10^4 ohms), the lead resistance must be subtracted for that temperature and frequency. As a result, the overall accuracy of the resistance measurement for any one frequency is estimated to be about 0.1 to 0.2 percent. In addition, however, a small polarization effect was always observed even for the platinum-sputtered crystals. It is estimated that the overall accuracy of the resistance measurements was about 0.4 to 0.5 percent.

Temperature Control and Measurement

The crystals were heated in a high-purity alumina tube such as shown in figures 1 and 2. The electrode and thermocouple leads exit by means of vacuum-tight insulators in the cooled top. The furnace is a three-zoned furnace in which each zone is controlled individually. Therefore, heat losses from the center section to the ends of the furnace can be minimized by maintaining the bottom and top of zones 1 and 3, respectively, at the same temperature as zone 2. Each zone is controlled by means of a saturable-core-reactor proportional control unit. Inductive effects from the furnace heating coils (alternating current) on the resistance measurements were minimized. First, the heating coils were wound noninductively. Second, the alternating-current power was switched to a rectified alternating current prior to observing the crystal resistance. This involved a full-wave bridge rectifier in conjunction with a resistance-capacitor filter network.

Since the platinum electrodes often stick to the crystals after heating to high temperatures, the thermocouple could not be placed directly on the crystal. Therefore, temperature gradients within the crystal and between the crystal and the thermocouple were minimized as shown in figure 2, which is an enlarged view of the crystal heating region. First, the three-zoned furnace maintained a relatively constant temperature profile within the region. Second, the crystal and thermocouple region is semienclosed by means of the outer round baffle and a baffle lid. Third, a series of baffles above the crystal region reduced heat losses to the cooler furnace top. Finally, the crystal was allowed to stay at the desired temperature for at least 1/2 hour before taking resistance measurements to ensure both temperature and thermodynamic equilibrium.

The electromotive force of the platinum - platinum-13-percent-rhodium thermocouple

was measured with a potentiometer, which was stated to be accurate to within 0.01 per-cent. This thermocouple had been calibrated (at the National Bureau of Standards) for a certainty of at least 0.5° up to 1100° C.

Measurement Procedure

The crystal was lowered into the furnace by means of the electrode leads (fig. 2); preheated to 250° to 400° C in vacuum to remove oxygen, adsorbed water, and other gaseous impurities; and then cooled to room temperature. Helium gas, which had been purified by passing over copper chips at 350° to 375° C and then slowly through a liquid-nitrogen trap, was added (and maintained) at a pressure of about 400 millimeters of mercury. Periodically, the system was reevacuated at higher temperatures to prevent the buildup of outgassing oxygen or water.

Most of the resistance measurements were taken after the temperature had been increased. Generally, this method is highly desirable if the temperature change is relatively large. The equilibrium number of defects, contributing to the conductivity, is a function of the temperature. Therefore, if resistances are measured as the temperature is decreased, the solid may contain more defects than those contained for equilibrium. The time required to reach equilibrium may be quite long, particularly if the temperature has been dropped too rapidly over a wide temperature range. Nevertheless, if care is taken to assure equilibrium, the resistance measurements can be made with either method; for example, similar resistance values were obtained for one crystal (B) where both heating and cooling methods were used.

RESULTS AND DISCUSSION

The general equation for the conductivity of barium fluoride was assumed to be

$$K_s = \frac{1}{R_s} = A \exp\left(-\frac{E}{RT}\right)$$

where

- K_s specific conductivity
- A factor
- E activation energy
- T absolute temperature

A plot of the specific conductivity (for both alternating- and direct-current measurements) against the reciprocal of the temperature (fig. 3) indicated the presence of two regions. The lower region is the extrinsic region, and the upper region, starting at about 210° C (1/T of about 0.00207) is the intrinsic region.

The extrinsic region is seen more clearly in figure 4, which contains direct-current measurements made on three crystals (A, B, and C). Only two of these crystals (A and B) showed an extrinsic region within the temperature ranges observed.

The activation energies for crystals A and B in the extrinsic region can be determined as follows:

$$E = -(\text{slope})(2.3026)(1.9865) \quad \text{cal}$$

The A-factor can then be calculated for each point:

$$A = \frac{K_s}{2.7183^{-E/1.9865T}} \quad \text{mhos}$$

Finally, the specific conductivities for crystals A and B can be represented, respectively, by their rate equations:

$$K_s = 0.58 \exp \left(-\frac{22\,000}{RT} \right) \quad \text{ohm}^{-1} \text{ cm}^{-1}$$

$$K_s = 1.3 \exp \left(-\frac{23\,000}{RT} \right) \quad \text{ohm}^{-1} \text{ cm}^{-1}$$

As shown in figure 3, the intrinsic region was essentially a straight-line function starting at about 210° C. A more careful observation indicates that an anomalous increase in the conductivity is obtained starting at about 670° C (1/T of ~ 0.00106). The slopes for crystals C and D are not constant (above 670° C), as shown in figure 5; instead, they are continuously curving to higher values. Crystal A, however, which had graphite surface coatings, does give the expected straight line at 10 kcps. In fact, the conductivity of crystal A fits closely the dotted line that was calculated from the rate equation for this upper intrinsic region for all of the samples. It is obvious that while crystal A is showing the expected conductivity, crystals C and D with platinum surfaces must have an additional contribution (probably electronic in nature) that is not a function of the crystal alone. Additional support for this supposition can be obtained by extrapolating the conductivities of C and D to the melting point. For example, an impossible

value of greater than $63 \text{ ohm}^{-1} \text{ cm}^{-1}$ would be obtained for fused barium fluoride at its melting point if those conductivities observed at 960°C for platinum surfaces were extrapolated. The reason for this additional contribution to the intrinsic conductivity of those crystals with platinum surfaces is not obvious since it is not an inherent function of the ionic conductivity of the crystal; however, it will not be considered further.

The intrinsic conductivity was expected to follow a single straight line essentially if the curving slope region (discussed previously) is disregarded. The plot for the alternating-current data for crystal D (1 kcps) between 400° and 670°C is shown in figure 6. Surprisingly, two straight lines were obtained, which suggests that more than one mechanism is operating. For simplicity the lower region, between 210° and 560°C , will be called the lower intrinsic region, and the upper region, between 560°C and the melting point, will be called the upper intrinsic region.

Some of the alternating-current data for the lower intrinsic region is shown in figure 7 for all four crystals. In this region, the specific conductivity of a single crystal should not depend on its purity or past history. Therefore, all similar crystals should give, essentially, the same conductivities. Basically, this has been observed. First, crystal A at 10 kcps and crystals B, C, and D at all three frequencies (100 cps, 1 kcps, and 10 kcps) have almost identical slopes; furthermore, the specific conductivities for A (at 10 kcps), B, and C are almost identical. Resistances in crystal B were obtained as the temperature was increasing and decreasing. Since the same line was obtained for both methods, an equilibrium number of defects was assumed to be present in both cases. It should be recognized, however, that if a crystal is cooled rapidly from high temperatures, a surplus of defects ("freezing-in") might result leading to higher conductivities. The conductivity of crystal D seems to be displaced slightly upward. After crystal D was heated to greater than 800°C and then cooled, its conductivity was reexamined as crystal D'. The conductivity of D' had dropped to values that were almost identical to those of A, B, and C. The explanation for the higher conductivity (higher A-factor) for crystal D prior to heating is not obvious. The specific resistance is obtained from the observed total resistance and the dimensions. Inaccuracies in these measurements cannot be the basic explanation since the measurements can be determined more accurately than the results indicate. A possible explanation is an observed consistent error of about 2.2°C . This seems highly unlikely since the conductivity dropped back to that of crystals A, B, and C after heating. Slight deviation from equilibrium seems to be a more reasonable explanation. Although this intrinsic region is not supposed to depend on the past history or purity, it is conceivable that a surplus of thermal defects, over that in equilibrium, may have been present in crystal D. After heating to greater than 800°C , the crystal was cooled slowly. Subsequent resistance measurements were made on crystal D' whose defects were at thermal equilibrium.

Polarization and its associated resistance effects are known for direct-current inves-

tigations. Polarization may also occur in alternating currents. When an alternating current is applied to a sample, the charge carriers move back and forth in phase with the applied voltage. When these carriers arrive at the electrodes, some of them may accumulate and produce a field. This field will hinder the approach of additional charges and tend to increase the resistance (ref. 7). In addition, it has been stated that blocking of the carriers at internal boundaries within the crystal may also produce similar effects (ref. 8). In this investigation, polarization effects were relatively small in crystals B, C, and D, which had platinum-sputtered surfaces. The resistances of each crystal changed only slightly with frequency. For example, the difference in the resistance for each crystal was only about 0.4 percent for frequencies of 100 cps to 10 kcps. Apparently, small polarization effects were obtained for crystal A, with graphite surface coatings, at 10 kcps since its resistance was almost identical to that for crystals B, C, or D', but crystal A gave considerable polarization at 1 kcps and 100 cps as shown by the increasing resistance. Therefore, only data at 10 kcps is considered representative for crystal A.

The slopes for crystals B, C, and D were calculated (by computer) along with their standard deviation errors. Since only two data points were available for crystal A at 10 kcps, no attempt was made to evaluate its error. The activation energies and the standard deviations were also calculated. These values are shown in table II. Since all barium fluoride single crystals should have the same activation energy in this lower intrinsic region, the best overall value of 32.7 kilocalories was assumed. The A-factor was then calculated for each resistance value. The average A-factor and its standard deviation are given in table II. It is obvious that crystals A (at 10 kcps), B, and C were almost identical and that crystal D had a slightly higher A-factor. Crystal D' (crystal D heated to over 800⁰ C) was almost identical to the others. By combining the data for crystals A (10 kcps only), B, C, and D', the conductivity of single crystals of barium fluoride in the lower intrinsic region can be represented by the following rate equation:

$$K_s = 3.78 \pm 0.09 \times 10^4 \exp \left(-\frac{32,700 \pm 500}{RT} \right) \quad \text{ohm}^{-1} \text{ cm}^{-1}$$

The upper intrinsic region for all barium fluoride crystals is given in figure 8. As in the lower region, crystals A (at 10 kcps), B, and C were almost identical, and crystal D was displaced upward by about the same amount as for the lower region. Although crystal D was not reexamined after heating, it seems certain that the conductivity of D' would be quite similar to that of A, B, and C.

The polarization effect for each crystal (B, C, or D) leads to an increase in the resistance of about 0.4 percent for a decrease in the frequency of 10 kcps to 100 cps. Crystal A showed a relatively small polarization effect at 10 kcps, but these effects were be-

coming quite large for 1 kcps and 100 cps. This was expected since the true resistances are becoming smaller in this region, and any additional resistances would be more noticeable.

The slopes and the activation energies for crystals A (10 kcps), B, C, and D are given in table III for this upper intrinsic region. The best overall activation energy of 35.6 kcal was assumed, and the A-factors calculated for crystals A, B, and C. As a result, the conductivity of barium fluoride single crystals in the upper intrinsic region can be represented by the following rate equation:

$$K_s = 2.05 \pm 0.03 \times 10^5 \exp \left(-\frac{35\,600 \pm 500}{RT} \right) \quad \text{ohm}^{-1} \text{ cm}^{-1}$$

It is believed that the conductivity in this upper region is essentially a monotonic function of the temperature up to the melting point. An extrapolation of this rate equation to the melting point of 1354°C (ref. 9) gives a specific conductivity of 3.43 mhos. Unfortunately, the conductivity of barium fluoride at its melting point is not known. This value, however, seems quite reasonable since the conductivity of calcium fluoride at its melting point is about 3.56 mhos (ref. 10).

SUGGESTED MECHANISMS FOR BARIUM FLUORIDE CONDUCTIVITY

Ionic halides, in general, are expected to conduct ionically rather than electronically. For example, the band gaps in cesium and lithium chlorides are 200 and 240 kilocalories, respectively (ref. 11). Therefore, barium fluoride is expected to be an ionic conductor since it should have a high band gap, since both its ions can have only one valency, and since it was handled in an inert atmosphere. As expected, transference numbers for solid barium fluoride indicated that it is an anionic conductor.

For ionic conductivity, ions must move through the crystal. In an ideal crystal, ions can migrate only by squeezing past each other, which requires energies of the order of 120 to 240 kilocalories (ref. 12). For real crystals, the observed energies are much less; for example, "pure" sodium chloride requires an activation energy of about 45 kilocalories. Therefore, ions must already be moving in real crystals, and the applied field (for conductivity studies) simply disturbs the statistical distribution of the motion by superimposing a directional component (ref. 13). Ion movement may occur in two ways. First, an ion may interchange with its neighboring species through a short-lived complex (ref. 14). This method is not considered as important for barium fluoride since the energy requirements would be too high. Second, an ion may move through imperfections in the "pure" barium fluoride crystal. Basically, there are three types of imperfections:

plane, line, and point. While it is recognized that planar and line imperfections may become more important for polycrystalline materials, it is believed that these effects are relatively minor in these single crystals at high temperatures. The point imperfections, on the other hand, involve individual ions and are probably of primary importance in the observed ionic conductivity of barium fluoride.

More than one type of point imperfection is possible; however, any mechanisms which involve transfer of barium ions can be eliminated since the solid conducts predominantly by fluorine ions. As a result, the imperfections, responsible for the fluoride migration, are probably of two types as shown in figure 9(b). It must be emphasized that figures 9(a) and (b) are only planar representations (for simplicity) of the ideal and real barium fluoride crystals and are not truly indicative of the crystal structure which is a fluorite type. Figure 9(b) shows how imperfections can lead to ionic mobility. First, an imperfection may be formed as both fluoride and barium ions (in a ratio of 2 to 1) move out of their normal sites and leave two types of defects: fluorine ion vacancies and barium ion vacancies (numbers 1 and 2 in fig. 9(b), respectively). Fluorine migration can occur, then, when another fluorine ion jumps into this fluorine vacancy. Of course, some barium ion migration should also be expected. It is believed that this type of imperfection is less important for barium fluoride. If this type of imperfection were controlling the conductivity, some barium ion mobility should be expected; for example, this type of mechanism has been suggested as being responsible for the mobilities in potassium chloride. The transport in potassium chloride at lower temperatures is principally by potassium ions. Still, at 500° C, the transference of the chlorine ion is about 6 percent, and as the temperature is increased to 600° C, the chloride transport increases to about 12 percent (ref. 2). This change in transport should be accompanied by a change in conductivity. Careful measurements of potassium chloride indicate that the slope of the intrinsic region does change because of the onset of anionic conductivity (ref. 15). Two intrinsic regions were also observed in barium fluoride starting at about 560° C. Although transference numbers have been measured only to 530° C (ref. 2), it seems certain that the transport is almost completely by fluorine ions up to much higher temperatures. For example, barium chloride is stated to be a pure anionic conductor up to at least 700° C (ref. 2). Finally, calcium fluoride, which should behave similarly to barium fluoride, has a calcium ion transport of less than 10^{-6} at 1000° C (ref. 5). Therefore, although this type of imperfection cannot be rejected absolutely, it appears highly unlikely that it contributes significantly to the conduction in barium fluoride.

The second type of point imperfection is significant in barium fluoride conductivity. This imperfection involves moving a fluorine ion into an interstitial and forming two defects: an interstitial fluorine ion and a fluorine ion vacancy (shown as number 3 in fig. 9(b)). Fluorine ions can then migrate by moving to different interstitial sites and vacancies. Whether one defect will predominate for a specific temperature range will depend on the respective energy relations for the two defects.

It has been intimated that two defects are responsible for the ionic conductivity in barium fluoride. These defects can be related directly to conductivity. For each imperfection, two defects are formed. The probability of forming imperfections in the intrinsic region is an exponential function of the temperature:

$$X_{F, Vac} X_{F, Int} \propto \exp \left(-\frac{F}{RT} \right)$$

where $X_{F, Vac}$ and $X_{F, Int}$ are the mole fractions of the fluorine vacancy and interstitials, respectively, and F is the free energy associated with formation. Since the number of defects that are produced thermally are much greater than those produced by impurities in this region, the following expressions are obtained

$$X_{F, Vac} X_{F, Int} \propto \exp \left(\frac{S}{R} \right) \exp \left(-\frac{H}{RT} \right)$$

and

$$n = n_0 \exp \left(-\frac{E_F}{2RT} \right)$$

where n is the number of interstitial or vacancy defects, n_0 is a constant, and E_F is the energy of formation of the defects. Ions must move if conductivity is to occur. The probability that a fluorine ion in an electric field will move into a vacancy next to it is also an exponential function of the temperature (ref. 16). The mobilities of the fluorine ions associated with the vacancy ($\mu_{F, Vac}$) and the interstitial ($\mu_{F, Int}$) can be expressed, respectively, as follows:

$$\mu_{F, Vac} = K_1 \exp \left(-\frac{E_{mig_{F, Vac}}}{RT} \right)$$

$$\mu_{F, Int} = K_2 \exp \left(-\frac{E_{mig_{F, Int}}}{RT} \right)$$

where K_1 and K_2 are constants and $E_{mig_{F, Vac}}$ and $E_{mig_{F, Int}}$ are the migration energies associated with the two defects. Thus, the specific conductivity K_s of barium fluoride in the intrinsic region is

$$K_S \propto n\mu$$

$$K_S = n_O \exp\left(-\frac{E_F}{2RT}\right) \left[K_1 \exp\left(-\frac{E \text{ mig}_{F, \text{Vac}}}{RT}\right) + K_2 \exp\left(-\frac{E \text{ mig}_{F, \text{Int}}}{RT}\right) \right]$$

The general equation derived for the intrinsic region indicated that two lines are possible. If it is assumed that the migration of the fluorine vacancy is controlling the lower intrinsic region, this general equation simplifies to

$$K_S = A_1 \exp\left(-\frac{E_L}{RT}\right)$$

where E_L is the observed activation energy for the lower intrinsic region and is equal to

$$E_L = \frac{E_F}{2} + E \text{ mig}_{F, \text{Vac}}$$

If it is assumed that the fluorine ion interstitial becomes more important and controlling in the upper region, the general equation simplifies to

$$K_S = A_2 \exp\left(-\frac{E_u}{RT}\right)$$

where E_u is the activation energy of the upper intrinsic region and is equal to

$$E_u = \frac{E_F}{2} + E \text{ mig}_{F, \text{Int}}$$

Unlike the intrinsic region, the extrinsic region is influenced by purity and past history (e. g., by surface effects) While surface effects may be of some importance in polycrystalline solids, it is considered to be of less importance here since single crystals of barium fluoride were used that were without visible flaws and were well annealed. Impurities, therefore, should control the number of defects in the extrinsic region. The type of defect depends on the impurity, as shown in figure 10. Again, it should be emphasized that figure 10 is only a simple planar representation of barium fluoride and is not a true indication of the crystal structure. If uranium trifluoride is added to barium fluoride, either fluorine ion interstitials or barium ion vacancies can be formed (fig.

10(a)). Density measurements indicate that the predominant defect is the fluorine interstitial (ref. 17). If sodium fluoride is added, either fluorine ion vacancies or sodium ion interstitials can be formed (fig. 10(b)). It has been shown that fluorine ion vacancies are found when sodium fluoride is added to calcium fluoride (ref. 18). The conductivity of barium fluoride in the extrinsic region should depend only on the mobilities of these defects since the number of defects remains constant. The general equation simplifies to

$$K_s = K_o \left[\exp \left(-\frac{E_{\text{mig}_F, \text{Vac}}}{RT} \right) + \exp \left(-\frac{E_{\text{mig}_F, \text{Int}}}{RT} \right) \right]$$

Since one defect predominates, the extrinsic region equation is

$$K_s = A_3 \exp \left(-\frac{E_E}{RT} \right)$$

where E_E is the observed activation energy for the extrinsic region and should be approximately equal to the migration energy of the dominant species.

The following energies were observed for barium fluoride:

- (1) Extrinsic region, $E_E = 23$ kcal
- (2) Lower intrinsic region, $E_L = 32.7$ kcal
- (3) Upper intrinsic region, $E_u = 35.6$ kcal

If it is assumed that the fluorine ion vacancy is controlling the conductivity in the extrinsic and lower intrinsic region, the migration energy of the vacancies is about 23 kilocalories, and the formation energy of the defects is about 20 kilocalories. As a result, the migration energy for fluorine ion interstitials in the upper intrinsic region is assumed to be about 26 kilocalories. These energies compare favorably with those migration energies (determined from the extrinsic regions) for fluorine ion vacancies and fluorine ion interstitials in calcium fluoride of about 18 to 14 kilocalories and 29 to 26 kilocalories, respectively (ref. 5).

Although it should be recognized that this supporting evidence is neither complete nor absolute, a mechanism for the conductivity of barium fluoride can be suggested that is both plausible and logical. First, the extrinsic region conductivity results from fluorine ion vacancies that are produced by impurities such as a monovalent fluoride (e. g., by an alkali fluoride). Second, the lower intrinsic region is a continuation of this controlling defect that is now produced thermally. Finally, the conductivity due to the fluorine ion interstitial defect becomes increasingly more important leading to the upper intrinsic region.

Lewis Research Center,

National Aeronautics and Space Administration,
Cleveland, Ohio, December 10, 1965.

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TABLE I. - RANDOM ANALYSIS OF
BARIUM FLUORIDE SINGLE
CRYSTALS

| Material | Percent by weight |
|------------|----------------------|
| Strontium | 0.5 |
| Potassium | .002 |
| Sodium | .002 |
| Oxygen | .002 |
| Calcium | .001 |
| Aluminum | .001 |
| Magnesium | .001 |
| Phosphorus | .0005 |
| Chloride | .0004 |
| Cobalt | .0003 |
| Iron | .0001 |

TABLE II. - SLOPES, ACTIVATION ENERGIES, AND A-FACTORS OF BARIUM
FLUORIDE SINGLE CRYSTALS FOR LOWER INTRINSIC REGION

| Crystal | Individual values | | Overall values | | |
|--|------------------------------|-------------------------------|---|-------------------------------|--|
| | Slope | Activation energy, kcal | Slope | Activation energy, kcal | A-factor |
| A | -6.93×10^3 | 31.6 | ----- | ^a 32.7 | ^a 3.72×10^4 |
| B | $-7.14 \pm 0.09 \times 10^3$ | 32.7 ± 0.4 | ----- | ^a 32.7 ± 0.4 | ^a $3.76 \pm 0.09 \times 10^4$ |
| C | $-7.01 \pm 0.06 \times 10^3$ | 32.1 ± 0.3 | ----- | ^a 32.7 ± 0.6 | ^a $3.78 \pm 0.08 \times 10^4$ |
| D | $-7.17 \pm 0.04 \times 10^3$ | 32.8 ± 0.2 | ----- | ^a 32.7 ± 0.5 | ^a $4.03 \pm 0.04 \times 10^4$ |
| D' | ----- | ----- | ^b -7.15×10^3 | ^b 32.7 | ^b 3.84×10^4 |
| Combined data for A, B, C, and D' | ----- | ----- | ^b $-7.15 \pm 0.09 \times 10^3$ | ^b 32.7 ± 0.5 | ^b $3.78 \pm 0.09 \times 10^4$ |

^aAssume best overall activation energy of 32.7 kcal for each crystal.

^bAssume values for crystal D' after heating D to $>800^\circ \text{C}$.

TABLE III. - SLOPES, ACTIVATION ENERGIES, AND A-FACTORS
OF BARIUM FLUORIDE SINGLE CRYSTALS FOR
UPPER INTRINSIC REGION

| Crystal | Individual values | | Overall values ^a | |
|-------------------------------|------------------------------|-------------------------|-----------------------------|-----------------------------|
| | Slope | Activation energy, kcal | Activation energy, kcal | A-factor |
| A (10-kcps frequency only) | -7.65×10^3 | 35.0 | 35.6 | 1.99×10^5 |
| B | $-7.77 \pm 0.10 \times 10^3$ | 35.6 ± 0.5 | 35.6 ± 0.5 | $2.05 \pm 0.02 \times 10^5$ |
| C | $-7.78 \pm 0.08 \times 10^3$ | 35.6 ± 0.4 | 35.6 ± 0.4 | $2.05 \pm 0.02 \times 10^5$ |
| D | $-7.74 \pm 0.08 \times 10^3$ | 35.4 ± 0.4 | ----- | ----- |
| Combined data for A, B, and C | ----- | ----- | 35.6 ± 0.5 | $2.05 \pm 0.03 \times 10^5$ |

^aAssume best overall activation energy of 35.6 kcal for each crystal.

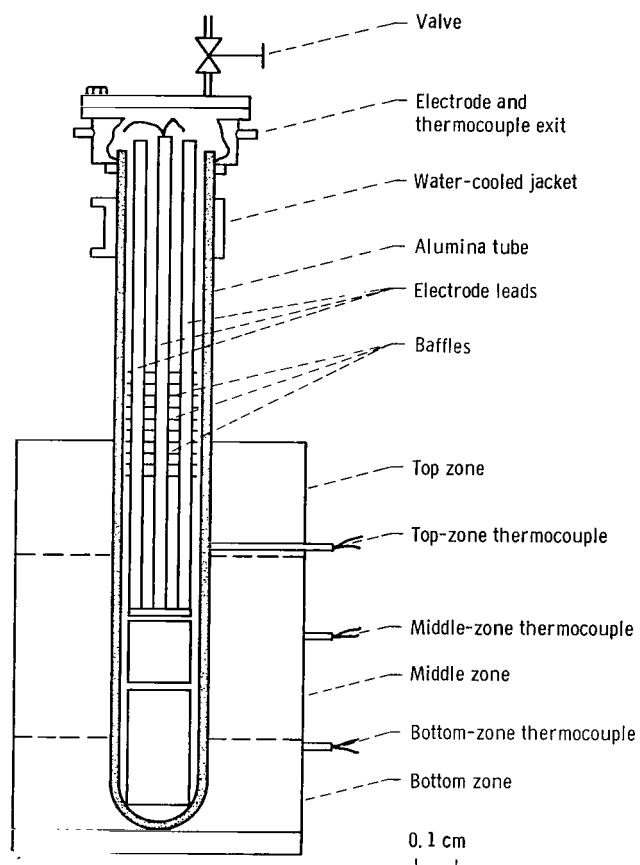


Figure 1. - Heating system.

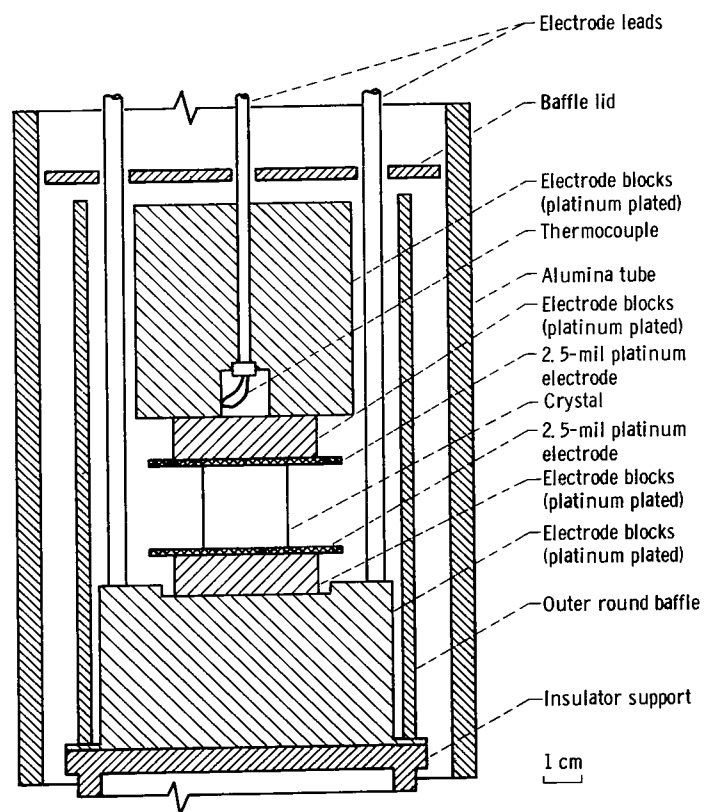


Figure 2. - Crystal area.

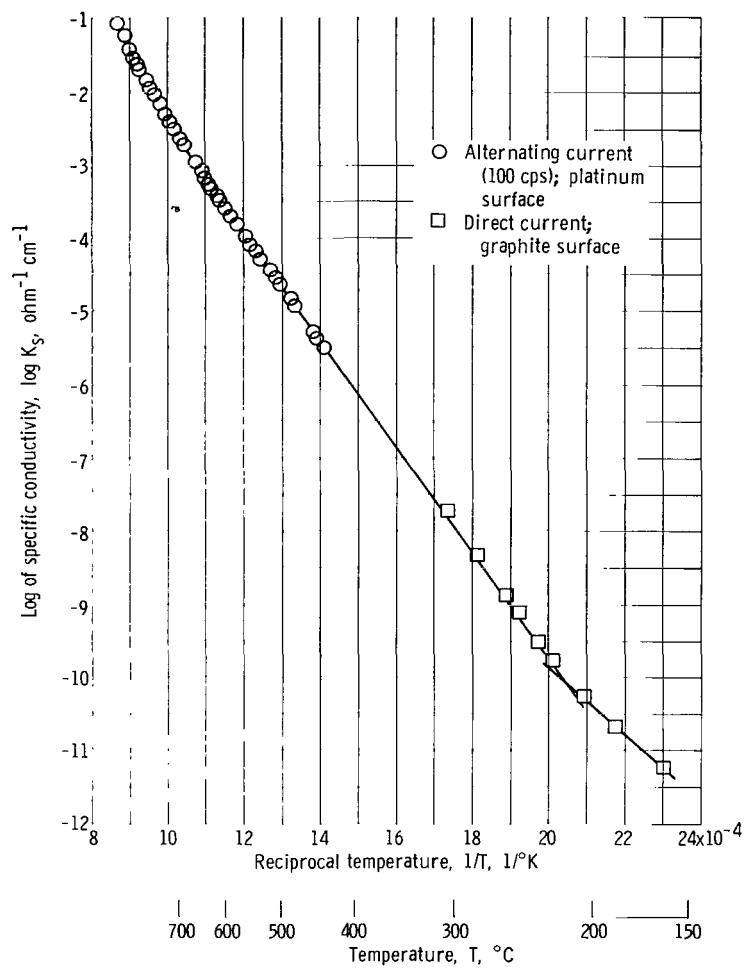


Figure 3. - Specific conductivity of barium fluoride single crystal.

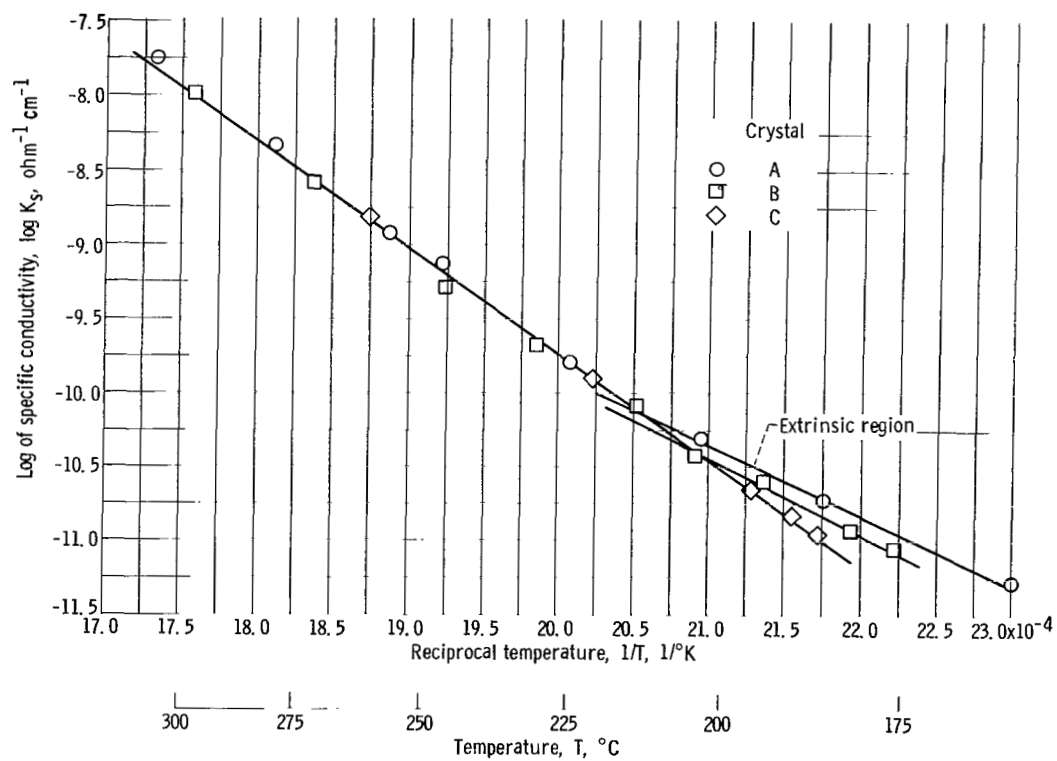


Figure 4. - Direct current measurements of barium fluoride crystals.

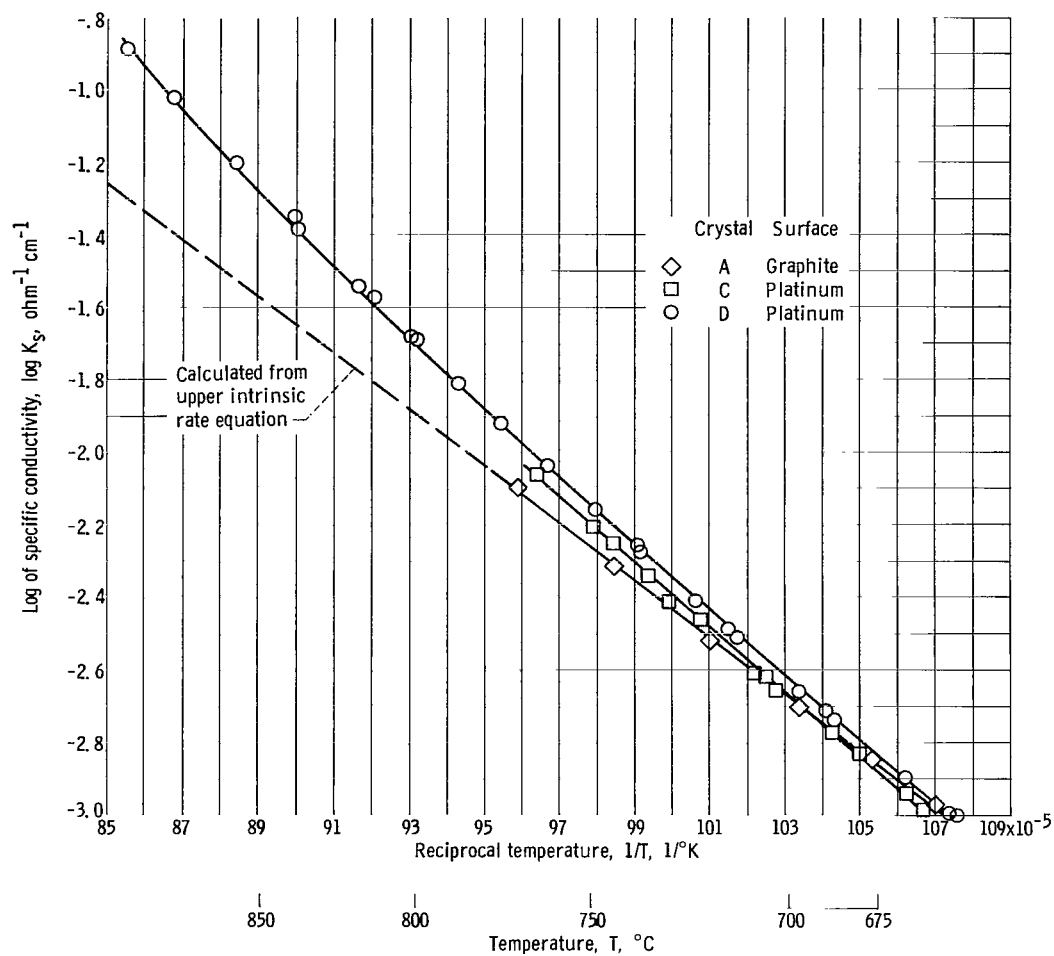


Figure 5. - Anomalous increase in specific conductivity of barium fluoride single crystals at temperatures above 670°C at a frequency of 10 kilocycles per second.

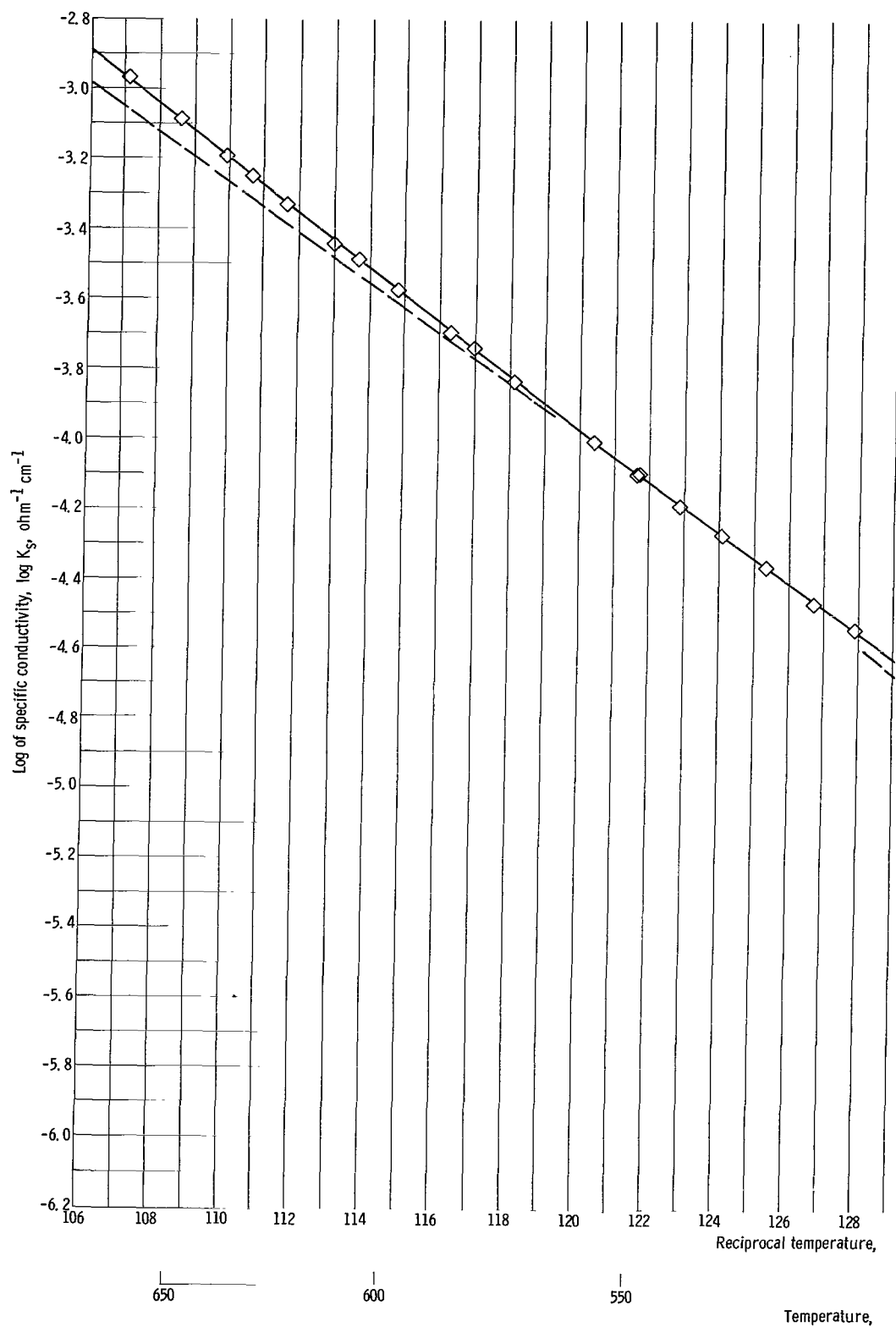
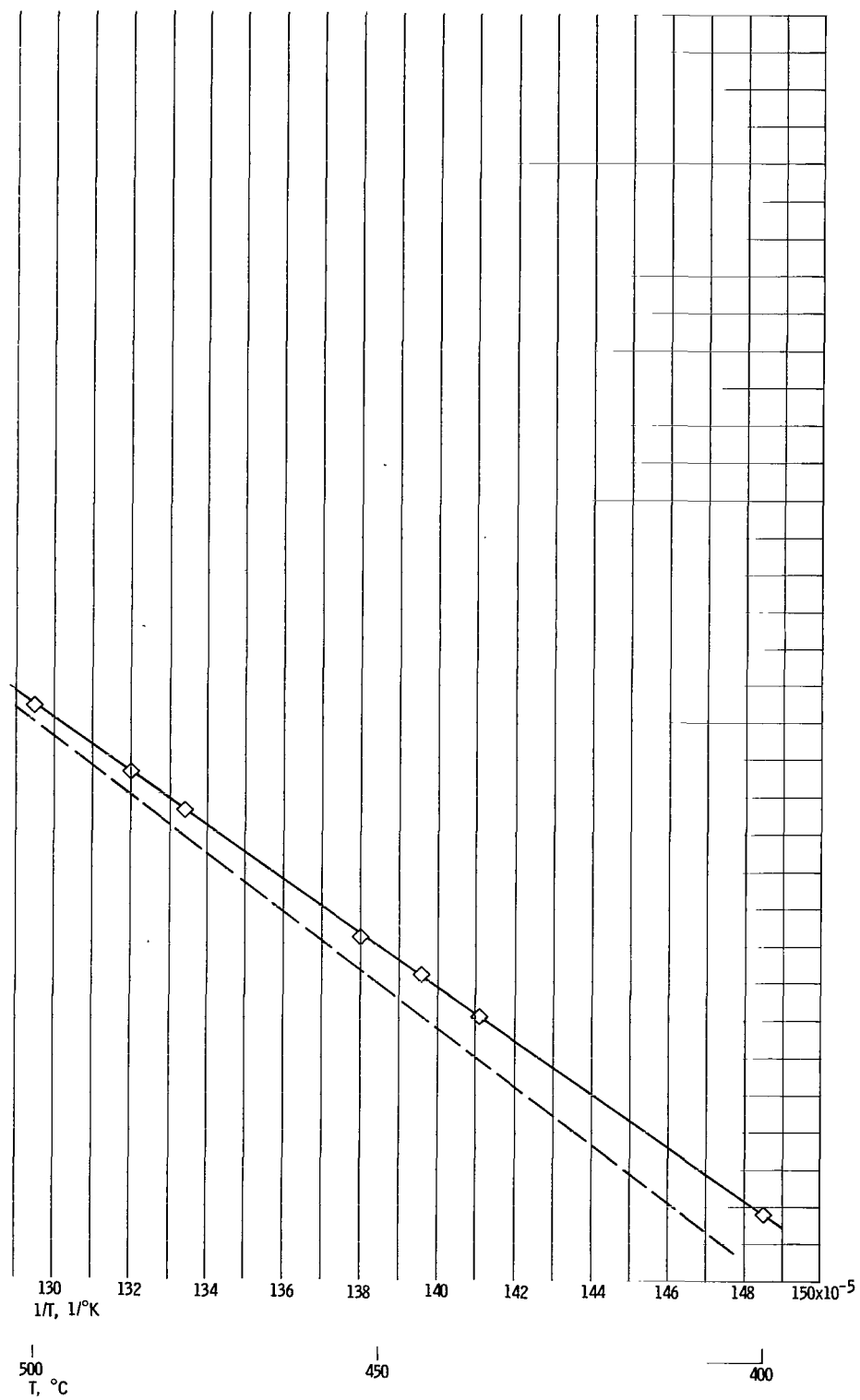


Figure 6. - Alternating current data for upper and lower intrinsic specific



conductivities of barium fluoride crystal D at frequency of 1 kilocycle per second.

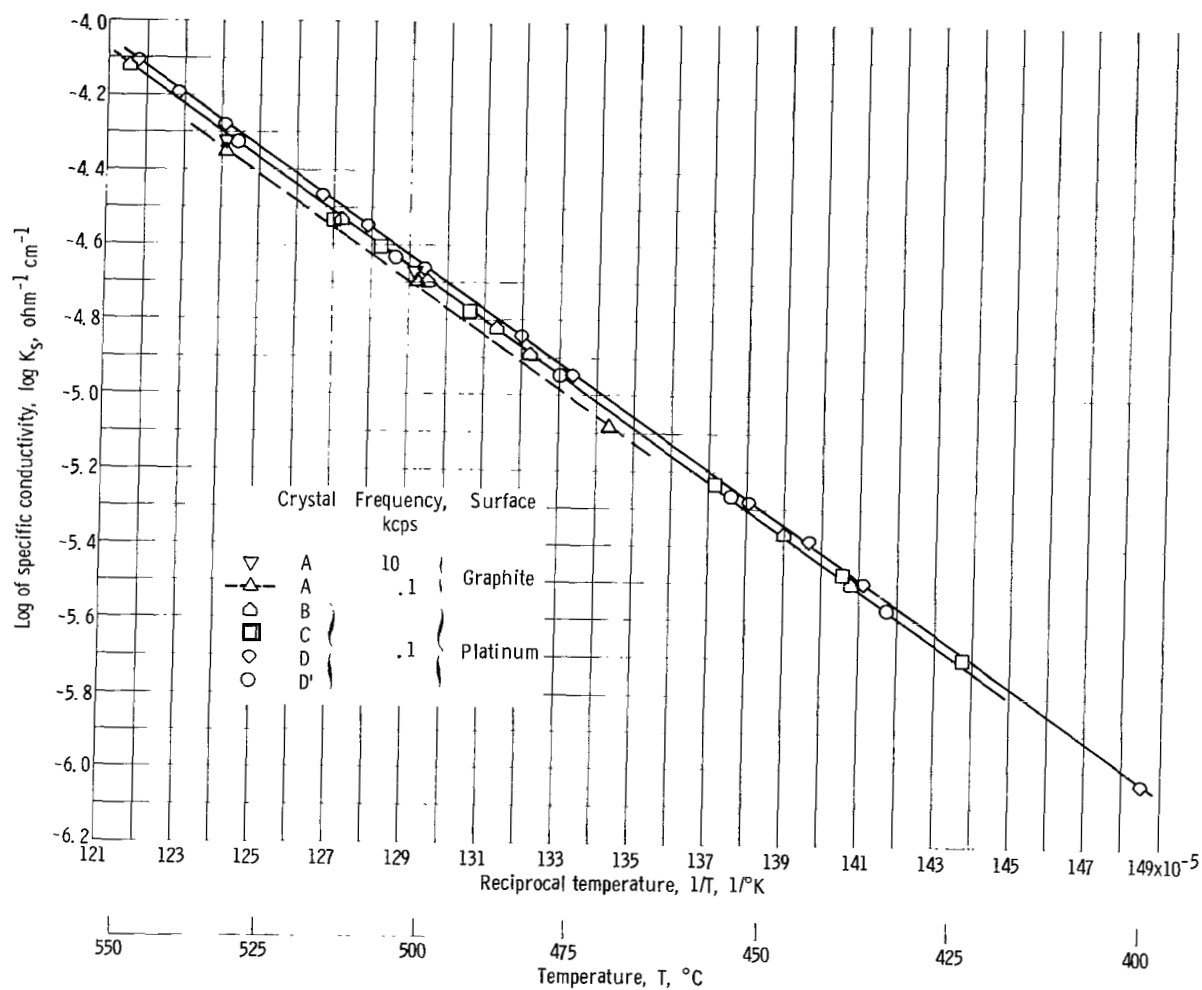


Figure 7. - Specific conductivities (alternating current) of barium fluoride in lower intrinsic region between temperatures of 400° to 560° C.

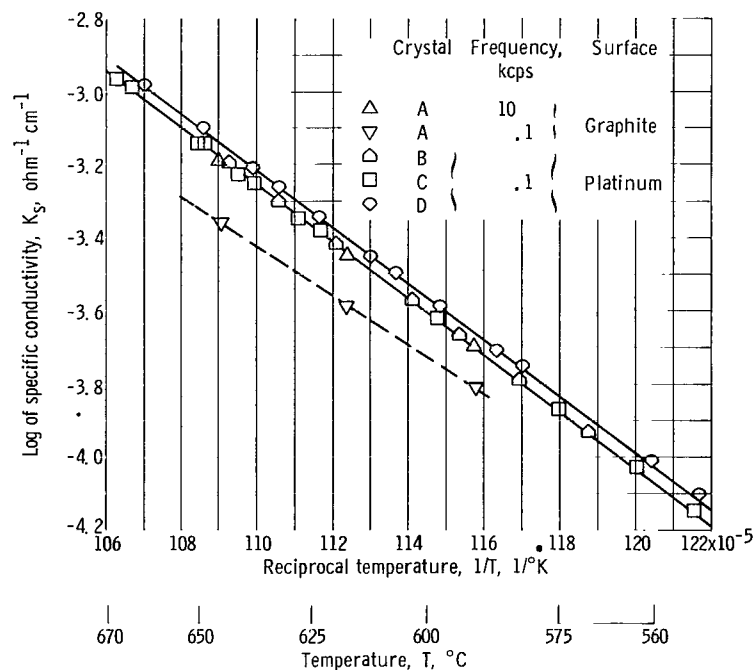


Figure 8. - Specific conductivity of barium fluoride for upper intrinsic region between temperatures of 560° to 670° C.

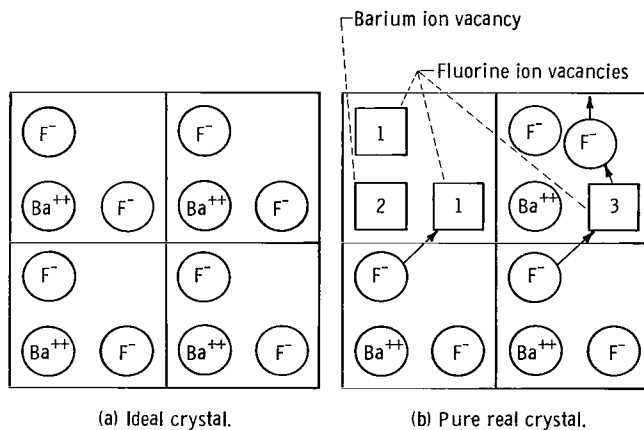
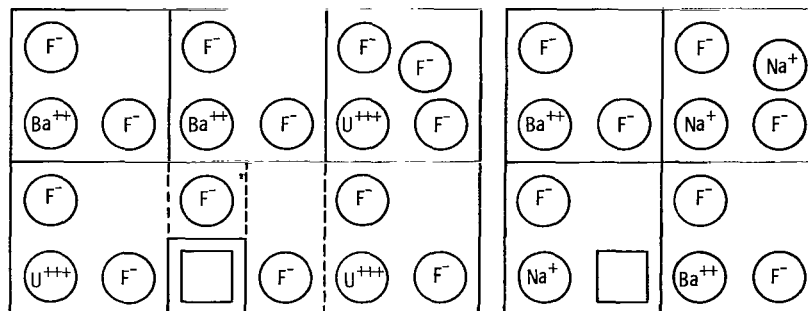


Figure 9. - Point defects in ideal and pure barium fluoride.



(a) Addition of trivalent fluoride (UF_3) to barium fluoride produces barium ion vacancies or fluorine ion interstitials.

(b) Addition of monovalent fluoride (NaF) to barium fluoride produces fluorine ion vacancies or sodium ion interstitials.

Figure 10. ~ Addition of impurities to barium fluoride to produce point defects.

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